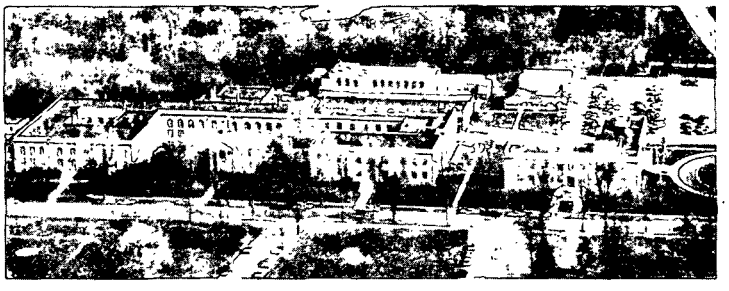

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 8

THE SOLUTION PROPERTIES OF METHYLOL CELLULOSE IN DIMETHYL SULFOXIDE

HAROLD A. SWENSON

MAY, 1975

THE SOLUTION PROPERTIES OF METHYLOL CELLULOSE IN DIMETHYL SULFOXIDE

Harold A. Swenson

INTRODUCTION

The discovery of a solvent which allows the immediate recovery of uncontaminated cellulose without degradation of either cellulose or solvent overcomes the great difficulty one has in isolating cellulose from an aqueous solution containing a metal, an amine and a high concentration of alkali. Because of the simplicity with which cellulose is recovered, the new solution process appears to mark the beginning of a significant advance in cellulose technology.

The new solution process seems destined to replace cuene for the routine determination of degree of polymerization with a considerable gain in accuracy and reliability. The actual time required for complete solution is only about three minutes followed by cooling before the viscosity measurement.

In the report which follows, a description is given of the experimental details required for the viscosity determination and reliable constants are provided for conversion of viscosity to DP.

This paper was presented at the Eighth Cellulose Conference at Syracuse, New York, May 19-23 (1975).

SYNOPSIS

Experimental details required for dissolution of cellulose with formaldehyde in dimethyl sulfoxide and details of the viscosity analysis are described. The intrinsic viscosity — DP relation $[\eta] = 3.38 \times 10^{-2} \times DP_w^{0.84}$ for methylol cellulose in DMSO, based on analysis of standard pulps and a kraft pulp is given. A density of 1.56 is found for methylol cellulose in DMSO* similar to that found for cellulose in water and other solvents. The apparent molar volume based on density is much less than the frictional volume. This is shown by plots of viscosity and the axial ratios as a prolate ellipsoid vs. DP_n. The intrinsic viscosity of methylol glucose and cellobiose for example is 2.5 times greater than for glucose and cellobiose in water. This difference between the apparent molar volume and the frictional volume, shown to persist to higher DP levels, illustrates that the frictional envelope is attached to the chain by secondary forces undetectable by density measurement. Viscosity and use of the ellipsoid model show that methylol cellulose in DMSO has high extension in solution, greater than does cellulose in cadoxene or FeTNa or than cellulose triacetate in dichloroethane. It is suggested that the water-clear solutions are suitable for light scattering, sedimentation and osmometry measurements. The new solvent offers clear advantages over currently used cellulose solvents because of the speed of dissolution, the absence of degradation, easy recoverability and the ability, apparently independent of accessibility, to dissolve kraft and holo pulps and high DP cotton.

---

*Traces of paraformaldehyde are found to persist in solution (1).

Solution Properties of Methylol Cellulose in Dimethyl Sulfoxide

by Harold A. Swenson

After reaction with formaldehyde, cellulose is converted to methylol cellulose which dissolves almost instantaneously in DMSO (1). In contrast to mixtures of amines with DMSO (2), solubility is so rapid as to appear unaffected by variations in accessibility of the fiber. High DP cotton, without prior treatment, dissolves as easily and completely as low DP pulp. Kraft (4% lignin) and holo pulps, apparently insoluble in cuene and cadoxene, also dissolve quickly.

Solutions of methylol cellulose in DMSO are very stable and the viscosity closely reproducible. Precipitation and recovery is done quickly with alcohol or water and after drying and redissolving, no loss in DP is found. The water-clear solutions are being used for light scattering and sedimentation analyses (3) and should be ideal for osmometry when appropriate noncellulosic membranes are available.

Formaldehyde can either be introduced as a gas (1), or be produced by decomposition of paraformaldehyde powder in DMSO at appropriate high temperatures. The latter method is used in the procedure which follows.

Experimental

Preparation of solutions

A crystallizing dish, 170 mm in diameter, containing silicone fluid at a depth of 25 mm is placed on a stirrer-hot plate and kept at 155°C at a level sufficient to cover two thirds of the depth of a small reaction vessel. The latter is a 15 ml capacity crystallizing dish with an outside ground glass cover. Small stirrers are prepared by inserting 12 mm lengths of iron wire into 2 mm ID glass tubing which is then sealed at the ends.

Ten mls of DMSO, 10 mg of cellulose and 0.5 g of paraformaldehyde powder are added to the tared dish and stirrer and the total weight recorded. The dish is then placed in the bath, a thermometer inserted, and vigorous stirring begun.

In a typical experiment the temperature rose to 87°C after one minute, to 105°C at 1 1/2 minutes and to 120°C in two minutes. At this point the formaldehyde bgan to bubble off violently. At the same time the cellulose sample quickly dissolved. Formaldehyde continued to bubble off and after two minutes the temperature was 128°C. In three minutes bubbling had largely subsided and the clear solution was removed and placed in a hood to cool and to dispel further formaldehyde vapor. After ten minutes the cover was replaced to hinder pickup of water.

The dish with cover is again weighed. In a typical experiment a weight loss of about 350 mg occurred. This was made up with DMSO-PF solution prepared exactly as was the original solution except for the absence of cellulose. Only a slight odor of formaldehyde remains.

The Viscosity Measurement

Intrinsic viscosities were determined in #100 Cannon-Ubbelohde semi-micro viscometers of one ml capacity at 30 $\pm$ 0.003°C. Dilutions of 0.2, 0.4, 0.6, 0.8, and 1.0 ml (to a final total of four ml) of DMSO-PF are added to obtain six concentration levels.

It was found that a linear extrapolation of the reduced viscosity plot was not obtained if anhydrous DMSO, unreacted with formaldehyde, was used as the diluting solvent. Later determinations (1) indicate that DMSO can be used as long as water is minimized.

RESULTS

The Viscosity — DP Relation of Methylol Cellulose in DMSO

The intrinsic viscosity of three ICCA (International Committee for Cellulose Analysis) pulps, 1, 4 and 5 and a kraft pulp of known DP were measured. The DP_w of the pulps found (4) by light scattering in the ferric tartrate solvent FeTNa were confirmed by sedimentation analysis of the trinitrate derivatives (5). A plot of log [η] vs. log DP_w of methylol cellulose in DMSO seen in Fig. 1, results in the relation $[\eta] = 3.38 \times 10^{-2} \times DP_w^{.84}$.

DP_w found by light scattering and sedimentation was further confirmed by viscosity measurement in FeTNa by use of the relation $[\eta] = 2.74 \times DP_w^{.78}$ (4). The latter constants for the viscosity-DP relation in FeTNa are closely similar to those for cadoxene (6) as are the persistence lengths in the two solvents (7).

As the higher constants suggest, methylol cellulose in DMSO is extended to a greater extent than is cellulose in FeTNa and cadoxene. This is illustrated in Fig. 2 by plots of the log viscosity -log DP_n relation from glucose to DP 100. Like plots for cellulose in cadoxene, cellulose triacetate in dichloroethane and for cellodextrins in water (8) are shown in the figure.

The beginning plateau of the curves in Fig. 2 occurs because the breadth is equal to or greater than the length of the frictional envelope. The increasing length of the chain then results in an abrupt increase in slope. For cellulose triacetate this occurs at about DP 6 where the frictional envelope, at least 33 A long, is apparently similar to its breadth. In contrast the plateau region for cellodextrins in water hardly extends to DP 2, while for cadoxene it extends to about DP 9 and for methylol cellulose in DMSO to about DP 11.

Comparison of the intrinsic viscosity of methylol glucose and methylol cellobiose in DMSO with unreacted glucose and cellobiose in DMSO and other

solvents is shown in Table 2. The intrinsic viscosity of methylol glucose and cellobiose in DMSO is only a little greater than is that of the unreacted monomer and dimer in DMSO but is 2.5 times that of glucose and cellobiose in water. The intermediate values for FeTNa and cadoxene in the table are seen to be similar. The differences in frictional volume persist to higher DP levels as seen in Fig. 2.

The Apparent Molar Volume of Methylol Cellulose in DMSO

The density of methylol cellulose in DMSO was determined in a Lipkin pycnometer for a low molecular weight (DP_n = 33) sample at various concentrations as shown in Fig. 3. To obtain the molar volume the extrapolated value d_o = 1.090 at c=0 in Fig. 3, was used in the expression $V_{mol} = M_n/d_0 - 1000\ d - d_0/Cd_o$ (9), where M_n is the number average molecular weight (DP_n x 192) and d is the density at concentration c, in moles per liter. The apparent molar volume of methylol cellulose in DMSO, V_{mol} = 4065, results in an apparent density 6336/4065 = 1.56. This is close to the value 1.55, found for cellulose in toluene and less than that found for cellulose in water (10).

The Frictional Dimensions of Methylol Cellulose in DMSO

The factor ν in the expression $\eta - \eta_o/\eta_o = \nu.c$ which is 2.5 for spheres, (11) has been evaluated as an increasing function for ellipsoids and related to the axial ratios a/b or b/a of prolate or oblate ellipsoids in table form (12). Values of ν were obtained from the relation $\nu = [\eta]\ (M_n/V_{mol}) = [\eta].d$ (12) in which the intrinsic viscosity is in ml/g and d = 1.56 was taken from the density of methylol cellulose found in DMSO.

Plots of the axial ratio vs. DP_n in Fig. 4 show increasing length of the slope as prolate ellipsoid from cellulose triacetate to cellulose in cadoxene, to methylol cellulose in DMSO, respectively. Values for the function

ν and the axial ratios for cellulose in cadoxene and for methylol cellulose are listed in Table 1.

It is seen in Fig. 4 that shear forces in the viscometer and the viscosity of the surrounding solvent (13) impose rodlike linearity up to a critical folding length where the slope decreases sharply. Folding of the chain is seen to occur at DP 18 for cellulose triacetate in dichloroethane, at DP 31 for cellulose in cadoxene and at or beyond DP 39 for methylol cellulose in DMSO, two times the folding length found for cellulose triacetate under similar shear conditions.

DISCUSSION

The density and apparent molar volume of methylol cellulose in DMSO is closely similar to that found for cellulose in water and other solvents. This is not unreasonable as a substitution of one methylol group per monomer unit determined for the methylol product (1) would not be expected to contribute greatly to the density. On the other hand, the frictional volume of methylol glucose is 2.5 times as great as glucose in water or than glucose pentaacetate in dichloroethane and, as the plots show, this difference persists to higher DP levels.

In consequence it appears that DMSO acts through forces which are strong enough to provide a frictional envelope but are not strong enough to be a part of the chain molecule. Increases in the hydrodynamic (viscosity) volume of sulfonated latex due to the electric double layer, are not detectable by light scattering (14). The lengthening of the frictional envelope of methylol cellulose in DMSO, however, should be detectable by angular dependence of light scattering even though the breadth of the envelope may not be. As sedimentation analysis is dependent upon frictional effects, contribution of the total hydrodynamic volume can be expected.

As monosubstitution apparently occurs at the exposed no. 6 carbon (1), increased rotational hindrance may occur between the 6 carbon of one glucose and the 2 carbon of the next in analogy to hindered rotation in biphenyls cited (15) to explain the great extension of cellulose trinitrate in solution. As there is absence of nitrate charge, and if no buttressing occurs from substitution at the 2 and 3 positions, a lower degree of extension as compared to cellulose trinitrate, is expected. It may be recalled that the other common solvents for cellulose, i.e., cupraammonium, cupriethylenediamine, cadoxene and FeTNa all involve metals which appear to complex with the 2 and 3 positions along the chain (16, 17).

In analogy to natural synthesis of cellulose in water below DP 6, where simultaneous crystallization and precipitation apparently occur (18), the high extension of the methylol cellulose chain in DMSO may lead to enhanced crystallinity and strength when precipitation occurs.

The rapid dissolution of methylol cellulose in DMSO, the absence of degradation and the ability to dissolve most pulp types at all DP levels apparently independent of accessibility, all offer clear advantages over earlier cellulose solvents. The water-clear solutions also lend themselves to light scattering, sedimentation and osmotic pressure measurements needed for the proper support of the viscosity measurement. A simple spinning or adhesives technology appears to be possible in the new solvent system.

REFERENCES

1. Johnson, D. C., Nicholson, M. D., and Haigh, F. C., 8th Cellulose Conference, Syracuse, N.Y., Symposium Edition, J. Polymer Sci. 1975.

2. Koura, A., Schleicher, H., and Burkart, P., Faserforsch. Textiltech 23 No. 3, 128 (1972).

3. Tiede, D., Thesis in progress. The Institute of Paper Chemistry, 1975.

4. Valtasaari, L., Paperi Puu 39, 243 (1957).

5. Swenson, H. A., Svensk Papperstidning 78, No. 2, 61 (1975).

6. Henley, D., Arkiv Kemi 18, 327 (1961).

7. Swenson, H. A., Tappi 56, 106 (1973).

8. Ihnat, M., and Goring, D. A. I., Can. J. Chem. 45, 2353 (1967).

9. Weissberger, A., Physical Methods in Organic Chemistry, Vol. 1, p. 1161 (1949).

10. Davidson, G. F., J. Textile Ind. 18, T175, T275 (1927).

11. Simha, R., J. Phys. Chem. 44, 25 (1940).

12. Scheraga, H. A., J. Chem. Phys. 23, 1526 (1955).

13. Forgacs, O. L., and Mason, S. G., J. Colloid Sci. 14, 457, 473 (1959).

14. Goring, D. A. I., J. Colloid Interface Sci. 22, No. 4, 371 (1966).

15. Swenson, H. A., Schmitt, C. A., and Thompson, N. S. J. Polymer Sci. 11C, 243 (1965).

16. Lindberg, B., and Swan, B. Acta Chem. Scand. 17, 913 (1963).

17. Bayer, G. F., Green, J. W., and Johnson, D. C., Tappi 48, 557 (1965).

18. Stockmann, V. E. Biopolymers 11 251 (1972).

TABLE I

COMPARISON OF INTRINSIC VISCOSITY, INCREMENTAL FACTOR μ AND AXIAL RATIOS AS A PROLATE ELLIPSOID, OF METHYLOL CELLULOSE IN DMSO WITH CELLULOSE IN CADOXENE

DP_n	$[\eta]^a$ DMSO-PF	$[\eta]$ Cadoxene	$\bar{\nu}^a$ DMSO-PF	$\bar{\nu}$ Cadoxene	a/b^a DMSO-PF	a/b Cadoxene
1	6.3	4.0	9.88	6.53	7.93	5.48
2	6.6	4.8	10.43	7.83	9.23	6.43
5	8.35	6.0	13.19		9.76	7.00
14.2	12.5	11.4	19.75	18.6	12.92	12.3
16	14.2	13.0	22.44	21.5	14.10	12.8
18.4	17.5	15.1	27.65	24.6	16.17	14.8
24.3	19.7	17.0	31.13	27.7	17.45	16.1
28.8	23.3	18.5	32.13	30.2	19.53	16.9
33.0		21.0		34.3		18.95
39.0	32.7	25.0	51.67	40.25	23.95	20.7
79.5		27.6		66.3		27.9
97.0		30.2		76.7		30.2

[a] The methylol product.

TABLE II

THE INTRINSIC VISCOSITY OF METHYLOL GLUCOSE AND CELLOBIOSE IN DMSO COMPARED TO GLUCOSE AND CELLOBIOSE IN WATER, DMSO AND OTHER SOLVENTS

	Intrinsic Viscosity, ml/gram					
Sample	DMSO-PF	DMSO	DMF	FeTNa	Cadoxene	Water
Glucose	6.25[a]	5.40	4.95	2.7	4.0	2.5
Cellobiose	6.60[a]	5.75		4.6	4.8	2.7

[a]Methylol glucose and methylol cellobiose.

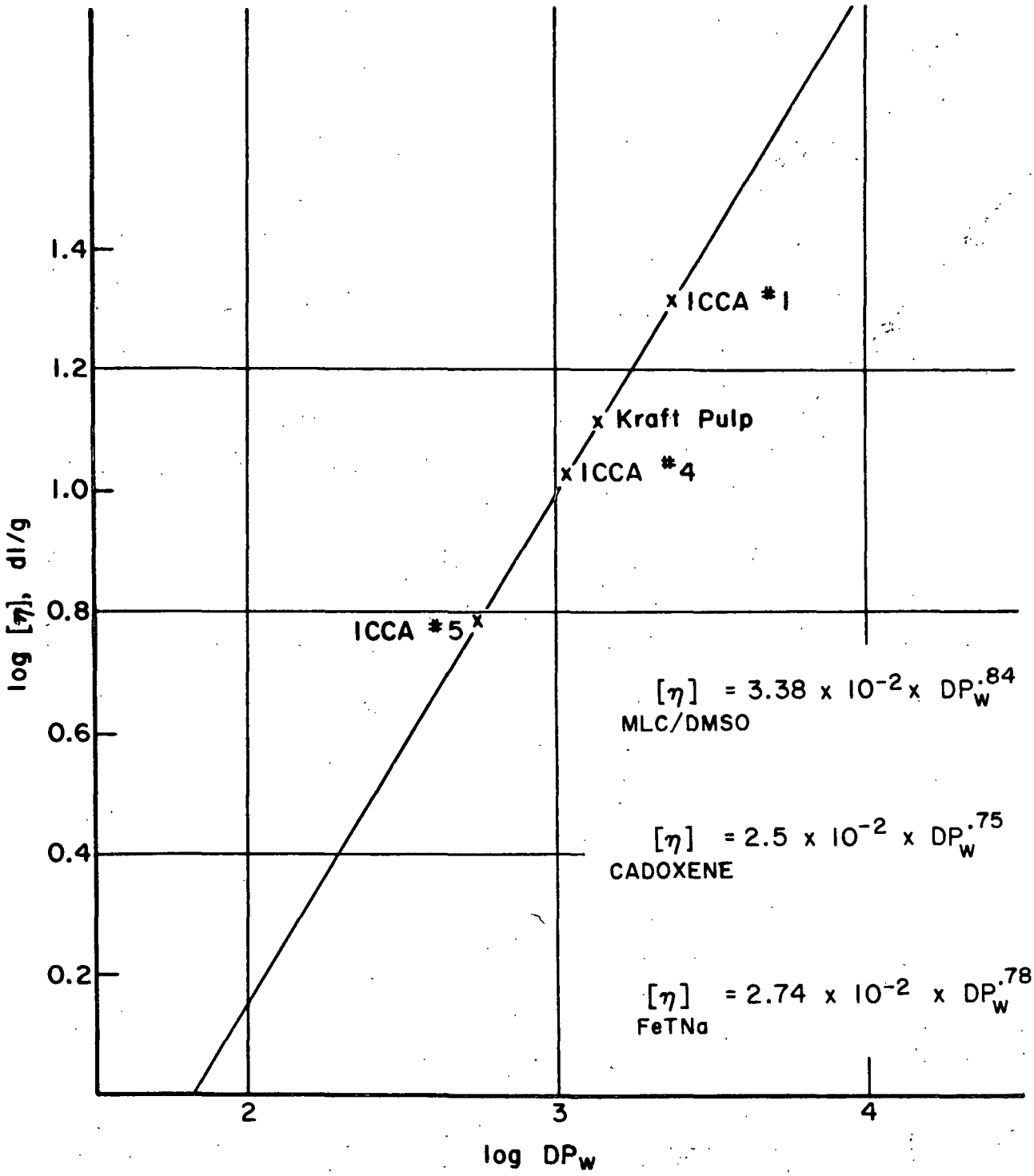

Figure 1. The logarithmic intrinsic viscosity vs. DP_w of methylol cellulose in dimethyl sulfoxide.

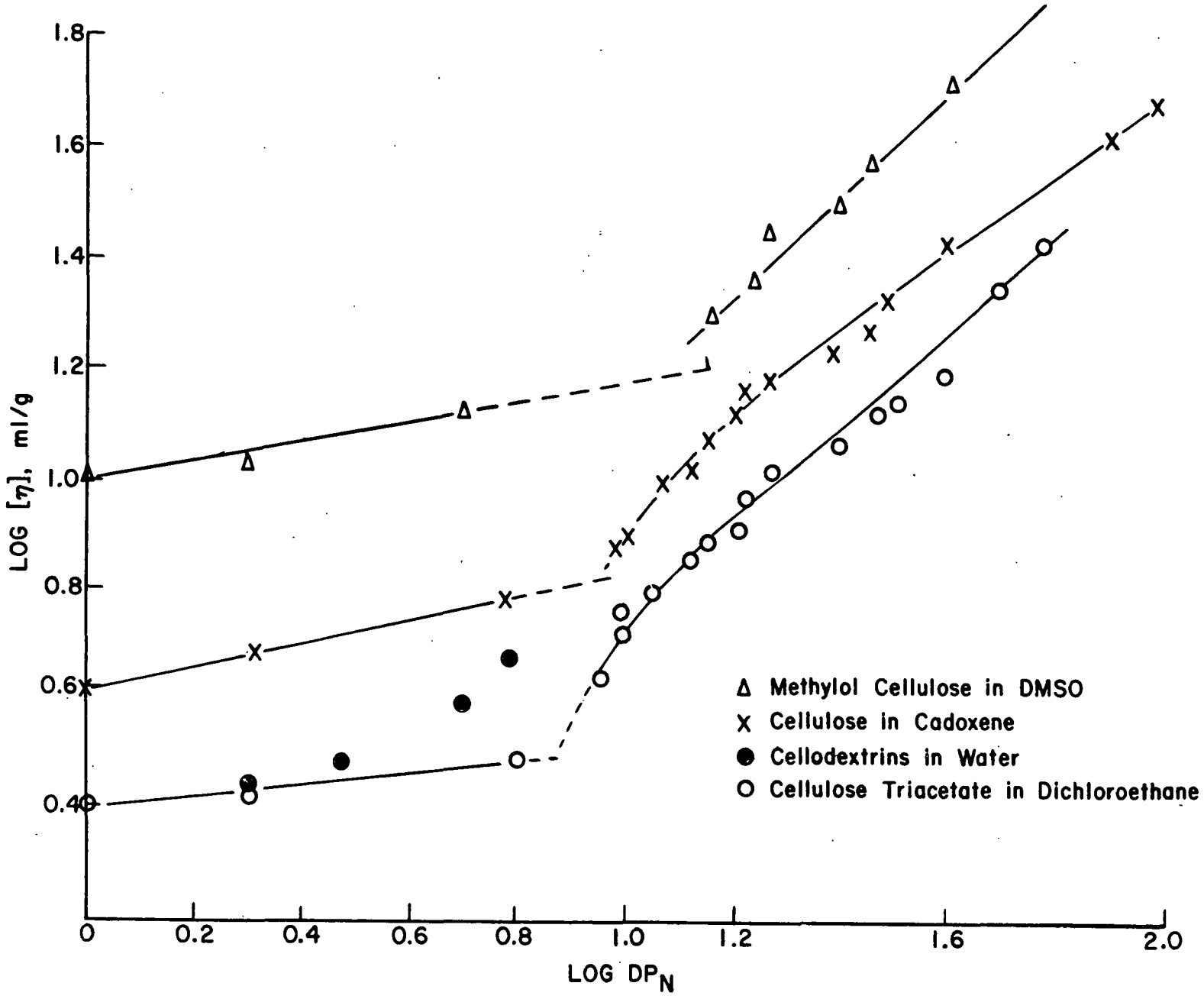

Figure 2. The logarithmic intrinsic viscosity vs. DP_n relation to cellodextrins to DP 38 compared to cellulose in cadoxene, cellodextrins in water and to cellulose triacetate in dichloroethane.

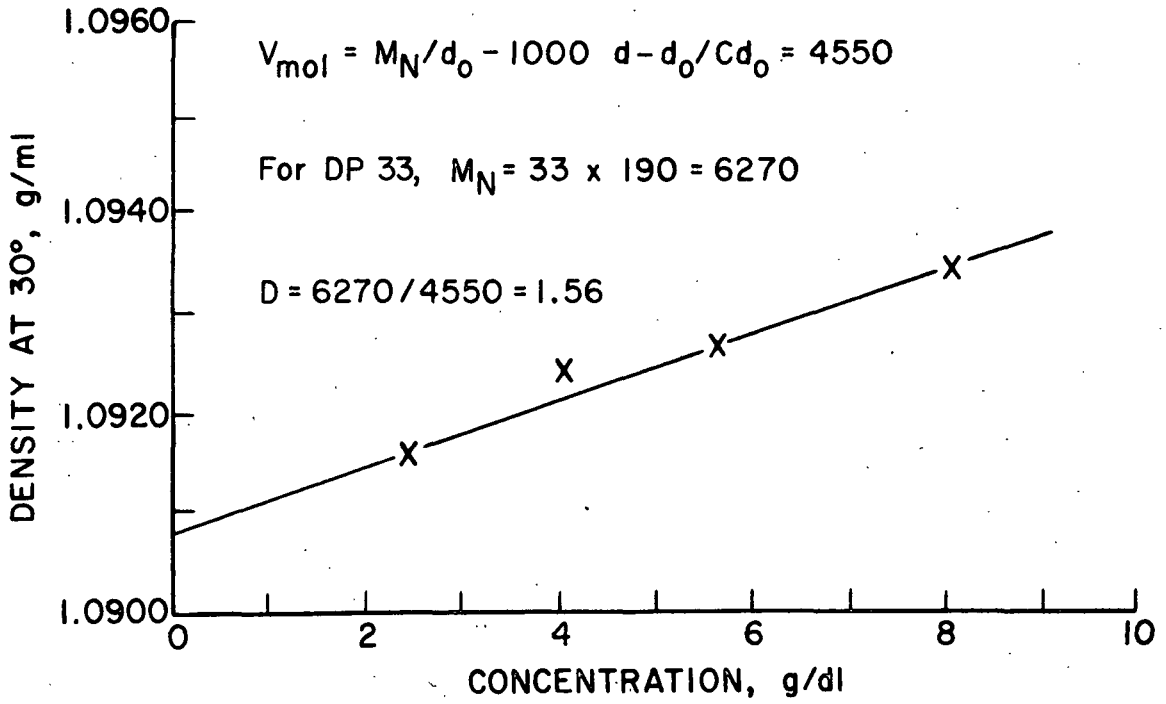

Figure 3. The density plot of DP 33 methylol cellulose in DMSO.

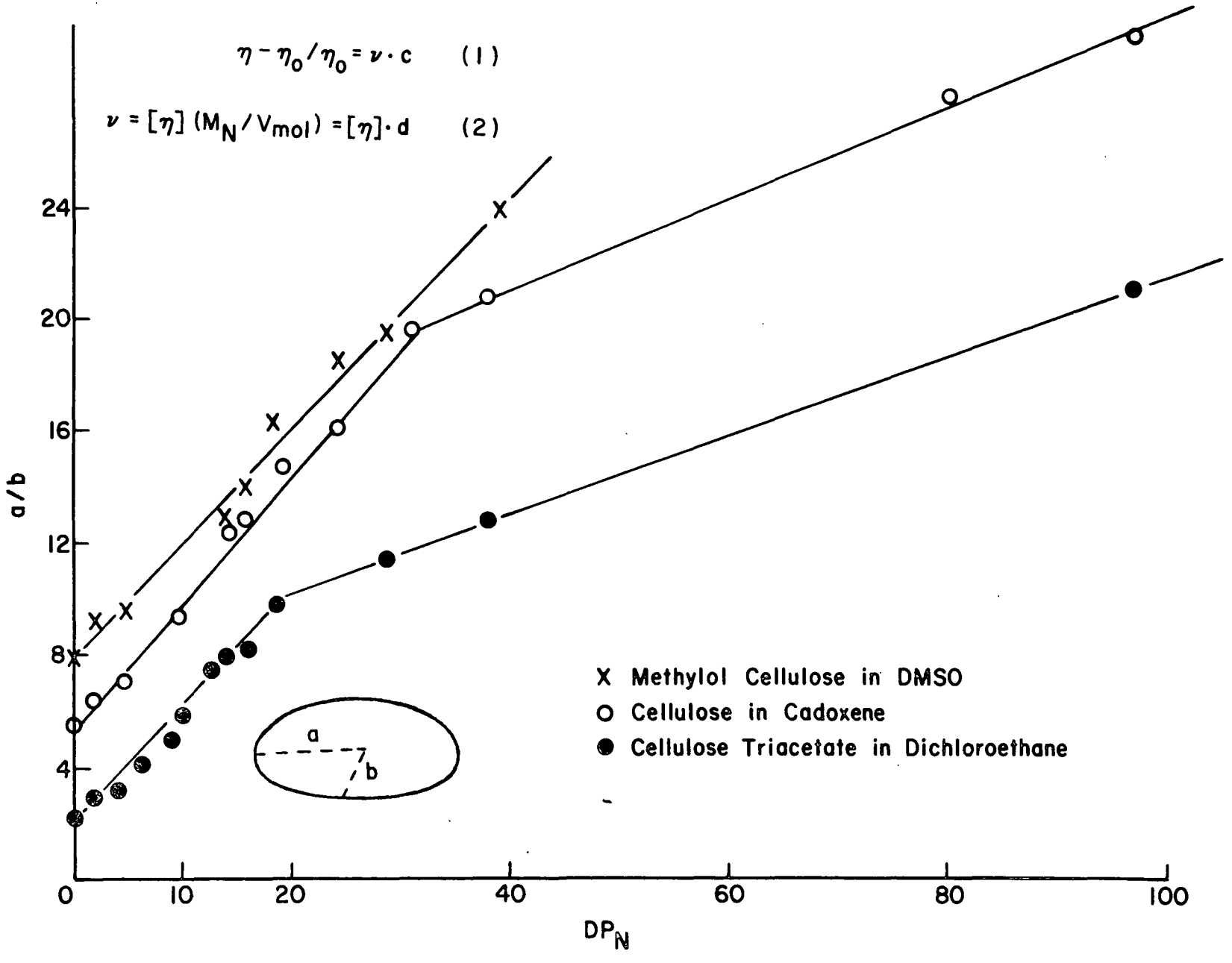

Figure 4. The axial ratio of methylol cellodextrins as a prolate ellipsoid to DP_n 38 compared to the ratios found for cellulose in cadoxene